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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 3/39, 17/06 — A1

(11) International Publication Number: **WO 98/11189**

(43) International Publication Date: 19 March 1998 (19.03.98)

(21) International Application Number: PCT/US96/14758

(22) International Filing Date: 13 September 1996 (13.09.96)

(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: BURNS, Michael, Eugene [US/US]; 7132 Valley Falls Court, Hamilton, OH 45011 (US). MASOTTI, Valentina [IT/IT]; Via Pertini, 5, I-40033 Casalecchio di Reno (IT). SARCINELLI, Luca [IT/IT]; Via S. Quasimodo, 65, I-00144 Rome (IT). SCIALLA, Stefano [IT/IT]; Via F.B. Rastrelli, 81, I-00128 Rome (IT).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: LAUNDRY PRETREATMENT PROCESS AND BLEACHING COMPOSITIONS

(57) Abstract

The present invention relates to a process for pretreating colored fabrics with a liquid composition comprising a C6-C20 aliphatic diacyl peroxide before washing said fabrics. This invention also discloses liquid compositions suitable for pretreating fabrics, having a pH of from 0 to 6, and comprising such an aliphatic diacyl peroxide and a second peroxygen bleach.

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LAUNDRY PRETREATMENT PROCESS AND BLEACHING COMPOSITIONS

Technical field

The present invention relates to bleaching compositions particularly suitable to be used as a pretreater, and to a process of pretreating fabrics.

Background

Peroxygen bleach-containing compositions typically based on hydrogen peroxide have been extensively described in laundry applications as laundry detergents, laundry additives or laundry pretreaters.

Indeed, it is known to use liquid compositions comprising hydrogen peroxide in laundry pretreatment applications. Although these liquid bleaching compositions provide good bleaching performance when used to pretreat a soiled fabric, there is still some room for further improvement regarding, for example, the stains/soils removal performance in pretreatment conditions.

Also a drawback associated with the direct application of neat liquid bleaching compositions onto fabrics, typically those comprising a high level of hydrogen peroxide, is that fabric dyes damage may occur, especially when these compositions are subsequently left to act onto the fabrics for prolonged periods of time before washing the fabrics. Indeed, when pretreating a fabric with such a bleaching composition, it is believed that a radical decomposition of hydrogen peroxide occurs on the surface of the fabric with generation of free radicals. It is further speculated that this

generation of free radicals may provide an aggressive decomposition of certain dyes present in the fabrics resulting in chemical damage of dye molecules, which is visible as discoloration and/or hue change. Thus, bleaching performance and fabric color safety are somewhat conflicting requir ments, but both are desirable in a single liquid composition for pretreating fabrics.

It is thus an object of the present invention to provide improved stain removal performance on a variety of stains/soils under pretreatment conditions, i.e., when a liquid bleaching composition is applied directly onto the soiled fabrics, and left to act onto said fabrics before they are washed, while delivering excellent bleaching performance.

It is a further object of the present invention to provide the previously mentioned advantage when pretreating fabrics with a liquid bleaching composition, while ensuring appropriate color safety to said fabrics, especially in those applications where said liquid composition is left neat into contact with said fabrics for prolonged periods of time before washing said fabrics.

It has now been found that the above objects can be met by using a liquid composition comprising a C6-C20 aliphatic diacyl peroxide to pretreat soiled fabrics. Indeed, it has been found that a C6-C20 aliphatic diacyl peroxide, in a liquid composition, delivers improved stain removal performance on fabrics under pretreatment conditions, as compared to the stain removal performance delivered by the same composition without said aliphatic diacyl peroxide. Also, it has been found that a C6-C20 aliphatic diacyl peroxide, in a liquid composition, reduces the color damage on colored fabrics under pretreatment conditions, as compared to the color damage observed with the same composition but with another peroxygen bleach like an aromatic diacyl peroxide, instead of said aliphatic diacyl peroxide. Thus, in its broadest aspect, the present invention encompasses a process for bleaching a fabric with a liquid composition comprising a C6-C20 aliphatic diacyl peroxide, said process comprising the steps of applying said composition in its neat form onto at least one portion of said fabric, optionally allowing said composition to remain in contact with said fabric, and then washing said fabric.

In the preferred embodiment of the present invention, it has been found that liquid compositions which are acidic, and comprise a C6-C20 aliphatic diacyl peroxide, and a second peroxygen bleach, provide improved stain removal performance and bleaching performance while ensuring appropriate color safety to said fabrics, especially when used under pretreatment conditions, as compared to the same compositions but without said aliphatic diacyl peroxide. Thus, the present invention also encompasses liquid acidic compositions comprising from 0.05% to 10% by weight of the total composition a C6-C20 aliphatic diacyl peroxide and from 0.01% to 10% by weight of a second peroxygen bleach. Furthermore, in a particularly preferred embodiment of the present invention the liquid compositions herein also comprise a bleach activator. Such compositions deliver more effective bleaching performance, especially at ambient temperature at which the pretreatment operation is performed.

An advantage of the present invention is that the improved stain removal performance obtained when pretreating fabrics according to the present invention is noticeable on a variety of stains/soils including enzymatic stains like blood, grass, and especially carotenoid-type stains like spaghetti sauce.

Another advantage of the liquid compositions according to the present invention is that they provide excellent performance when used in other applications apart from laundry pretreater application, such as in other laundry applications, as a laundry detergent or laundry additive, or even hard surface cleaning applications.

EP-A-687 726 discloses an aqueous composition in the form of an emulsion comprising two nonionic surfactants with different HLB and benzoyl peroxide. These compositions are suitable to pretreat fabrics. No aliphatic diacyl peroxides are disclosed.

European patent applications number 95870018.9, 95870051.0 and 95870082.5 disclose laundry bleaching compositions respectively containing chelating agents, radical scavengers and polyamines, and which are safe to colors and fabrics. The peroxygen bleaches disclosed therein

include peroxy acids such as diperoxydodecandioic acid but no aliphatic diacyl peroxides are disclosed.

European patent application number 95870051.0 discloses acidic liquid hard-surface compositions (pH 0 to 6) comprising sulphuric acid, surfactants, chelants and a peroxygen bleach as an optional ingredient. Dilauroyl peroxide is expressly disclosed amongst the peroxygen bleaches. No compositions comprising an aliphatic diacyl peroxide together with a second peroxygen bleach is exemplified.

EP-A-717 102 discloses liquid automatic dishwashing compositions comprising solvents, chelants and a diacyl peroxide of formula R-CO-OO-CO-R1, wherein R and R1 are the same or different, preferably no more than one is a hydrocarbyl chain of longer than 10 carbon atoms and more preferably at least one has an aromatic nucleus. These compositions may further comprise bleaches and bleach activators and are formulated at a pH of 7 to 13.

EP-A-106 584 discloses granular compositions containing (a) an halogenated peroxybenzoic acid or a peroxycarboxylic acid (R=C5-C18) and (b) a bleach activator (R=C5-C17) that contains a carbonyl carbon atom that can potentially react with such peroxybenzoic acid or a peroxycarboxylic acid to form a diacyl peroxide. No laundry pretreatment application is disclosed.

Summary of the invention

The present invention encompasses a process of bleaching a fabric with a liquid composition comprising an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, said process comprising the steps of applying said composition in its neat form onto at least a portion of the fabric, before said fabric is washed.

The present invention encompasses a liquid acidic composition suitable for pretreating fabrics, having a pH of from 0 to 6, and comprising from 0.05% to 10% by weight of the total composition of an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, and from 0.01% to 10% by weight of the total composition of a second peroxygen bleach.

Detailed description of the invention

The laundry pretreatment process

In its broadest embodiment the present invention relates to a process of pretreating a fabric with a liquid composition comprising an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms.

By "pretreating a fabric" it is to be understood that the liquid composition herein is applied in its neat form onto a soiled fabric, optionally left to act onto said fabric typically for a period of time of 1 minute to several hours, preferably 1 minute to 1 hour, and more preferably 1 minute to 30 minutes, before said fabric is washed, as described hereinafter, in the process of bleaching fabrics according to the present invention.

The present invention is based on the finding that a liquid bleaching composition comprising a C6-C20 aliphatic diacyl peroxide, when used to pretreat a soiled colored fabric, delivers improved stain removal performance on various stains like enzymatic stains, carotenoid-type stains and the like, while ensuring appropriate color safety to fabrics.

Indeed, the damage of some kinds of dyes present on fabrics, such as bleach sensitive dyes or metallized dyes, i.e., the color change and/or decoloration, observed when pretreating such a colored fabric with a liquid composition comprising a C6-C20 aliphatic diacyl peroxide, is reduced, as compared to the color change and/or decoloration observed when using, for example, the same composition but with an aromatic diacyl peroxide (e.g., benzoyl peroxide) instead of said aliphatic diacyl peroxide. This color change

and/or decoloration reduction is observed even if the composition is left to act onto the fabric upon prolonged periods of time before washing said fabric, e.g., about 24 hours.

It is speculated that reduced color damage on fabrics observed herein under pretreatment conditions is due to the much lower reactivity of free radicals generated from aliphatic diacyl peroxide versus, for example, those generated from aromatic diacyl peroxide. Indeed, the presence of such a C6-C20 aliphatic diacyl peroxide, in a liquid composition suitable to be used as a pretreater, provides excellent stain removal performance and excellent bleaching performance and does not have any negative effect on the dyes generally present on the surface of colored fabrics such as bleach sensitive dyes and/or metallized dyes including copper-formazan dyes and/or metal-azo dyes. In contrast, it has been observed that the radicals generated from the decomposition of aromatic diacyl peroxide like benzoyl peroxide cause color damage onto fabrics.

The stain removal performance and color damage of a composition on a fabric under pretreatment conditions may be evaluated by the following test method. A composition according to the present invention is first applied on a fabric, preferably on the stained portion of said fabric, left to act thereon from about 1 to about 10 minutes, preferably 5 minutes, after which the pre-treated fabric is washed according to common washing conditions, at a temperature of from 30°C to 70°C for a period of time sufficient to bleach said fabric.

The stain removal performance may be evaluated by comparing side by side the soiled colored fabric pre-treated with the composition according to the present invention with those pre-treated with the reference, e.g., the same compositions but without any aliphatic diacyl peroxide. For example, typical stains to be used in such a stain removal test method are commercially available from EMC (Empirical Manufacturing Company) Cincinnati, Ohio, USA, such as grass, spaghetti sauce, dirty motor oil, make-up, barbecue sauce, blood on two different substrate/fabric, e.g., cotton (CW120) and polycotton (PCW28). A visual grading scale may be used to assign differences in panel score units (psu), in a range from 0 to 4 for the stain removal performance.

The color damage may be evaluated by comparing side by side the soiled colored fabric pre-treated with the composition according to the present invention with those pre-treated with the reference, e.g., the same compositions but with an aromatic diacyl peroxide instead of an aliphatic diacyl peroxide. Technical colored swatches/fabrics suitable to be used in the color damage test method herein, are commercially available from EMC (Empirical Manufacturing Company) Cincinnati, Ohio, US. Typical colored fabrics/swatches used are for example the most sensitive to bleach like: C83 Reactive Blue®, C102 Reactive Blue®, C65 Reactive Violet®, C73 Direct Blue®, C105 Direct Brown®, C111 Direct Red®, C40 Sulphur Green®. A visual grading and/or instrumental methods with the "Hunterlab Tristimulus MINISCAN" may be used for the color damage evaluation.

Accordingly, the present invention encompasses a process of bleaching a fabric with a liquid composition comprising an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, said process comprising the steps of applying said composition in its neat form onto at least a portion of said fabric, optionally allowing said composition to remain in contact with said fabric preferably without leaving said composition to dry onto said fabric, before said fabric is washed.

Said liquid composition may remain in contact with said fabric, typically for a period of 1 minute to several hours, preferably 1 minute to 1 hour, more preferably 1 minute to 30 minutes, and most preferably 2 to 10 minutes. Optionally, when the fabric is soiled with encrusted stains/soils which otherwise would be relatively difficult to remove, said compositions may be rubbed and/or brushed more or less intensively, for example, by means of a sponge or a brush or simply by rubbing two pieces of fabric each against the other.

By "washing" it is to be understood herein to simply rinse the fabrics with water, or the fabrics may be washed with a conventional detergent composition comprising at least one surface active agent, this by the means of a washing machine or simply by hand.

By "in its neat form" it is to be understood that the liquid compositions are applied directly onto the fabrics to be pre-treated without undergoing any dilution, e.g., the compositions according to the present invention are applied as described herein.

According to the process of pretreating soiled fabrics of the present invention, the liquid compositions according to the present invention used in said process should preferably not be left to dry onto the fabrics. Indeed, it has been found that water evaporation contributes to increase the concentration of free radicals onto the surface of the fabrics and, consequently, the rate of chain reaction. It is also speculated that an auto-oxidation reaction occurs upon evaporation of water when the liquid compositions are left to dry onto the fabrics. Said reaction of auto-oxidation contributes to generate peroxy-radicals which may cause color damage. Thus, not leaving the present liquid bleaching compositions to dry onto the fabrics, in the process of bleaching fabrics according to the present invention, contributes to a benefit according to the present invention, i.e., to reduce color damage when pretreating fabrics with liquid bleaching compositions.

As an essential element the compositions to be used according to the present invention comprise an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, or mixtures thereof. It has been found that said aliphatic diacyl peroxides do not only contribute to the color safety profile of a liquid composition comprising them, when pretreating fabrics, but further contribute to the skin safety profile of said composition, i.e., that only limited skin itching or even no skin itching at all is observed when said composition is in contact with the skin of the user.

Preferred aliphatic diacyl peroxides are according to the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 4 to 18 carbon atoms, preferably from 6 to 16 and more preferably from 8 to 14.

Suitable aliphatic diacyl peroxides for use herein include dilauroyl peroxide, didecanoyl peroxide, dimyristoyl peroxide or mixtures thereof, and more preferred herein is dilauroyl peroxide.

Dilauroyl peroxide may be commercially available from AKZO Nobel under the trade name Laurox®.

Typically, the compositions suitable to be used according to the present invention comprise from 0.05% to 10% by weight of the total composition of such an aliphatic diacyl peroxide or mixtures thereof, preferably from 0.1% to 3%, more preferably from 0.3% to 2% , and most preferably from 0.5% to 1%.

The compositions used according to the present invention may further comprise another peroxygen bleach on top of said aliphatic diacyl peroxide, hereinafter called "second" peroxygen bleach. Other optional ingredients may further be added in said compositions herein like bleach activators, surfactants, brighteners, chelating agents, radical scavengers, stabilisers, soil suspending polyamine polymers, polymeric soil release agents, dye transfer agents, solvents, dyes, amines, catalysts, perfumes, or mixtures thereof. Preferred optional ingredients are further described in more details hereinafter.

The compositions used according to the process of the present invention are preferably aqueous compositions. The compositions used in the process herein have a pH of from 0 to 12, and are preferably formulated in the acidic pH range, typically at a pH between 0 and 6, and more preferably between 1 and 6. Acidic compositions are preferred herein for stability reasons. Also, formulating the compositions to be used in the process of the present invention in the acidic pH range, especially in the embodiment herein where said compositions further comprise a second peroxygen bleach, further contributes to the color safety profile of said compositions.

The compositions

The present invention also encompasses a liquid acidic composition suitable for pretreating fabrics, having a pH of from 0 to 6, and comprising from

0.05% to 10% by weight of the total composition of an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, and from 0.01% to 10% by weight of a second peroxygen bleach.

Thus, as an essential element the compositions according to the present invention comprise a C6-C20 aliphatic diacyl peroxide or mixtures thereof, as described hereinbefore.

As another essential element the compositions according to the present invention comprise a second peroxygen bleach or mixtures thereof. The second peroxygen bleach to be used herein is any peroxygen bleach, apart from said aliphatic diacyl peroxide, known to those skilled in the art. Such peroxygen bleaches include hydrogen peroxide, or a water-soluble source thereof, or mixtures thereof. Hydrogen peroxide is most preferred to be used in the compositions according to the present invention. Indeed, the presence of the second peroxygen bleach, preferably hydrogen peroxide, contributes to the excellent cleaning and bleaching benefits of the compositions according to the present invention. As used herein a hydrogen peroxide source refers to any compound which produces perhydroxyl ions when said compound is in contact with water.

Suitable water-soluble sources of hydrogen peroxide for use herein include percarbonates, persilicate, persulphate such as monopersulfate, perborates, peroxyacids such as diperoxydodecandioic acid (DPDA), magnesium perphtalic acid, perlauric acid, perbenzoic and alkylperbenzoic acids, hydroperoxide like t-butyl hydroperoxide and mixtures thereof.

The compositions according to the present invention comprise from 0.01% to 10% by weight of the total composition of such a second peroxygen bleach or mixtures thereof, preferably from 0.5% to 8%, more preferably from 2% to 8%, and most preferably from 4% to 7%.

It is by combining such an aliphatic diacyl peroxide with a second peroxygen bleach like hydrogen peroxide, in a liquid acidic composition, that excellent stain removal performance and outstanding bleaching performance

are obtained under pretreatment conditions, while ensuring appropriate color safety to said fabrics.

The compositions of the present invention are preferably aqueous liquid compositions. Said aqueous compositions are formulated in the acidic pH up to 6, preferably at a pH from 1 to 6, more preferably from 2 to 6, and most preferably from 3 to 5. Formulating the compositions of the present invention in the acidic pH range contributes to the stability of said compositions. Furthermore, it has surprisingly been found that formulating the compositions of the present invention in the acidic pH range contributes to the benefit of the present invention, i.e., ensuring appropriate color safety to a fabric under pretreatment conditions. The pH of the compositions of the present invention can be adjusted by using organic or inorganic acids known to those skilled in the art. Particularly suitable organic acids to be used herein are aryl and/or alkyl sulfonate, such as methane sulfonic acid or naphtalene disulfonic acid, citric acid, succinic acid, sulphamic acid, glutaric acid, adipic acid and the like. Particularly suitable inorganic acids are sulfuric acid, phosphoric acid, nitric acid and the like.

Optionals

The compositions according to the present invention may further comprise optional ingredients like bleach activators, surfactants, brighteners, chelating agents, radical scavengers, stabilisers, soil suspending polyamine polymers, polymeric soil release agents, dye transfer agents, solvents, dyes, amines, catalysts, perfumes, or mixtures thereof.

As an optional but highly preferred ingredient, the compositions of the present invention comprise a bleach activator or mixtures thereof. By "bleach activator", it is meant herein a compound which reacts with hydrogen peroxide to form a peracid. The peracid thus formed constitutes the activated bleach. Particularly suitable bleach activators to be used herein are hydrophobic bleach activators, i.e., a bleach activator which is not substantially and stably miscible with water. Typically, such hydrophobic bleach activators have a secondary HLB (hydrophilic lipophilic balance) below 11, preferably below 10. Secondary HLB is known to those skilled in the art and is defined for example in "Emulsions theory and

practice" by P. Becher, Reinhold, New York, 1957, or in "Emulsion science" by P. Sherman, Academic Press, London, 1969.

Suitable bleach activators to be used herein include those belonging to the class of esters, amides, imides, or anhydrides. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Suitable examples of such compounds to be used herein are tetracetyl ethylene diamine (TAED), sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS). Also suitable are N-acyl caprolactams selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam or mixtures thereof. A particular family of bleach activators of interest was disclosed in EP 624 154, and particularly preferred in that family is acetyl triethyl citrate (ATC). Acetyl triethyl citrate has the advantage that it is environmental-friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. Finally, it provides good building capacity to the composition.

The compositions according to the present invention may comprise from 0.01% to 10% by weight of the total composition of a bleach activator, or mixtures thereof, preferably from 0.5% to 10%, and more preferably from 3% to 7%.

The compositions according to the present invention may comprise a surfactant or mixtures thereof. Any surfactant known to those skilled in the art may be used herein including anionic surfactants, nonionic surfactants, zwitterionic surfactants, amphoteric surfactants and/or cationic surfactants up to a level of 50% by weight of the total composition.

The compositions according to the present invention may be formulated as solutions, emulsions or microemulsions.

For stability reasons, the compositions according to the present invention that may typically comprise a bleach activator, as described hereinbefore, are preferably formulated either as aqueous emulsions of said bleach activator in a matrix comprising water, the aliphatic diacyl peroxide, the second peroxygen bleach and an emulsifying surfactant system, or as microemulsions of said bleach activator in a matrix comprising water, the aliphatic diacyl peroxide, the second peroxygen bleach and a hydrophilic surfactant system.

Preferred peroxygen bleach-containing emulsions herein comprise an emulsifying surfactant system of at least two different surfactants, i.e., at least a hydrophobic surfactant having an HLB up to 9.5 or mixtures thereof, and at least a hydrophilic surfactant having an HLB above 10, or mixtures thereof, in order to emulsify the hydrophobic bleach activator. Preferred herein, said two different surfactants should have different HLB values (hydrophilic / lipophilic balance) in order to form stable emulsions, and preferably the difference in value of the HLBs of said two surfactants is at least 1, preferably at least 2. Indeed, by appropriately combining at least two of said surfactants with different HLBs in water, emulsions will be formed which do not substantially separate into distinct layers, upon standing for at least two weeks at 40°C.

The preferred emulsions according to the present invention comprise from 1 % to 50 % by weight of the total composition of said hydrophilic and hydrophobic surfactants, more preferably from 5 % to 40 % and most preferably from 8 % to 30 %. The preferred emulsions according to the present invention comprise at least from 0.01 % by weight of the total emulsion of said hydrophobic surfactant, or mixtures thereof, preferably at least 2 % and more preferably at least 4 % and at least from 0.01 % by weight of the total emulsion of said hydrophilic surfactant, or mixtures thereof, preferably at least 2%, and more preferably at least 4%.

The hydrophilic surfactants having an HLB above 10 to be used in said emulsions herein are preferably hydrophilic nonionic surfactants having an HLB above 10 and more preferably above 10.5. Preferred to be used herein

as the hydrophobic surfactants are the hydrophobic nonionic surfactants. Said hydrophobic nonionic surfactants to be used herein have an HLB up to 9.5, preferably below 9.5, more preferably below 9. Indeed, the hydrophobic nonionic surfactants to be used herein have excellent grease cutting properties, i.e., they have a solvent effect which contributes to hydrophobic soils removal.

Suitable nonionic surfactants for use herein include alkoxylated fatty alcohols preferably, fatty alcohol ethoxylates and/or propoxylates. Indeed, a great variety of such alkoxylated fatty alcohols are commercially available which have very different HLB values (hydrophilic / lipophilic balance). The HLB values of such alkoxylated nonionic surfactants depend essentially on the chain length of the fatty alcohol, the nature of the alkoxylation and the degree of alkoxylation. Hydrophilic nonionic surfactants tend to have a high degree of alkoxylation and a short chain fatty alcohol, while hydrophobic surfactants tend to have a low degree of alkoxylation and a long chain fatty alcohol. Surfactant catalogs are available which list a number of surfactants including nonionics, together with their respective HLB values.

Suitable chemical processes for preparing the nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well-known to the man skilled in the art and have been extensively described in the art. As an alternative, a great variety of alkoxylated alcohols suitable for use herein is commercially available from various suppliers.

Preferred hydrophobic nonionic surfactants to be used in the emulsions according to the present invention are surfactants having an HLB up to 9 and being according to the formula $RO-(C_2H_4O)_n(C_3H_6O)_mH$, wherein R is a C_6 to C_{22} alkyl chain or a C_6 to C_{28} alkyl benzene chain, and wherein n+m is from 0.5 to 5 and n is from 0 to 5 and m is from 0 to 5 and preferably n+m is from 0.5 to 4.5 and, n and m are from 0 to 4.5. The preferred R chains for use herein are the C_8 to C_{22} alkyl chains. Accordingly, suitable hydrophobic nonionic surfactants for use herein are Dobanol® 91-2.5 (HLB= 8.1; R is a mixture of C_9 and C_{11} alkyl chains, n is 2.5 and m is 0), or Lutensol® TO3 (HLB=8; R is a mixture of C_{13} and C_{15} alkyl chains, n is 3 and m is 0), or Tergitol® 25L3 (HLB= 7.7; R is in

the range of C_{12} to C_{15} alkyl chain length, n is 3 and m is 0), or Dobanol ^{R} 23-3 (HLB = 8.1; R is a mixture of C_{12} and C_{13} alkyl chains, n is 3 and m is 0), or Dobanol ^{R} 23-2 (HLB = 6.2; R is a mixture of C_{12} and C_{13} alkyl chains, n is 2 and m is 0), or mixtures thereof. Preferred herein are Dobanol ^{R} 23-3, or Dobanol ^{R} 23-2, Lutensol ^{R} TO3, or mixtures thereof. These Dobanol ^{R} surfactants are commercially available from SHELL. These Lutensol ^{R} surfactants are commercially available from BASF and these Tergitol ^{R} surfactants are commercially available from UNION CARBIDE. Other suitable hydrophobic nonionic surfactants to be used herein are non alkoxylated surfactants. An example is Dobanol ^{R} 23 (HLB < 3).

Preferred hydrophilic nonionic surfactants to be used in the emulsions according to the present invention are surfactants having an HLB above 10 and being according to the formula $RO-(C_2H_4O)_n(C_3H_6O)_mH$, wherein R is a C_6 to C_{22} alkyl chain or a C_6 to C_{28} alkyl benzene chain, and wherein n + m is from 5 to 11 and n is from 0 to 11 and m is from 0 to 11, preferably n + m is from 6 to 10 and, n and m are from 0 to 10. Throughout this description n and m refer to the average degree of the ethoxylation/propoxylation. The preferred R chains for use herein are the C_8 to C_{22} alkyl chains. Accordingly, suitable hydrophilic nonionic surfactants for use herein are Dobanol ^{R} 23-6.5 (HLB = 11.9 ; R is a mixture of C_{12} and C_{13} alkyl chains, n is 6.5 and m is 0), or Dobanol ^{R} 25-7 (HLB = 12 ; R is a mixture of C_{12} to C_{15} alkyl chains, n is 7 and m is 0), or Dobanol ^{R} 45-7 (HLB = 11.6 ; R is a mixture of C_{14} and C_{15} alkyl chains, n is 7 and m is 0), or Dobanol ^{R} 91-5 (HLB = 11.6 ; R is a mixture of C_9 to C_{11} alkyl chains, n is 5 and m is 0), or Dobanol ^{R} 91-6 (HLB = 12.5 ; R is a mixture of C_9 to C_{11} alkyl chains, n is 6 and m is 0), or Dobanol ^{R} 91-8 (HLB = 13.7; R is a mixture of C_9 to C_{11} alkyl chains, n is 8 and m is 0), or Dobanol ^{R} 91-10 (HLB = 14.2 ; R is a mixture of C_9 to C_{11} alkyl chains, n is 10 and m is 0), or mixtures thereof. Preferred herein are Dobanol ^{R} 91-10, or Dobanol ^{R} 45-7, Dobanol ^{R} 23-6.5, or mixtures thereof. These Dobanol ^{R} surfactants are commercially available from SHELL.

Apart from the hydrophilic nonionic surfactants other hydrophilic surfactants may further be used in the emulsions of the present invention such as

anionic surfactants described hereinafter and/or polyhydroxy fatty acid amide surfactant, or mixtures thereof, according to the formula

$$R^2 - C(O) - N(R^1) - Z,$$

wherein R^1 is H, or C_1-C_4 alkyl, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_5-C_{31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof.

Preferably, R^1 is C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl and most preferably methyl, R^2 is a straight chain C_7-C_{19} alkyl or alkenyl, preferably a straight chain C_9-C_{18} alkyl or alkenyl, more preferably a straight chain C_{11}-C_{18} alkyl or alkenyl, and most preferably a straight chain C_{11}-C_{14} alkyl or alkenyl, or mixtures thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2-(CHOR')(CHOH)-CH_2OH$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $CH_2-(CHOH)_4-CH_2OH$.

In the formula $R^2 - C(O) - N(R^1) - Z$, R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. $R^2 - C(O) - N<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide and the like. Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl and the like.

Suitable polyhydroxy fatty acid amide surfactants to be used herein may be commercially available under the trade name HOE® from Hoechst.

Methods for making polyhydroxy fatty acid amide surfactants are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed for example in GB patent specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., US patent 2,965,576, issued December 20, 1960 to E.R. Wilson, US patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, US patent 1,985,424, issued December 25, 1934 to Piggott and WO92/06070, each of which is incorporated herein by reference.

The emulsions according to the present invention may further comprise other surfactants on top of said emulsifying surfactant system, which should however not significantly alter the weighted average HLB value of the overall emulsion.

In a particularly preferred embodiment of the emulsions of the present invention, wherein the emulsions comprise acetyl triethyl citrate as the bleach activator, an adequate surfactant system, would comprise a hydrophobic nonionic surfactant with for instance an HLB of 6, such as a Dobanol ^{R} 23-2 and a hydrophilic nonionic surfactant with for instance an HLB of 15, such as a Dobanol ^{R} 91-10. Other suitable nonionic surfactant systems comprise for example a Dobanol ^{R} 23-6.5 (HLB about 12) and a Dobanol ^{R} 23 (HLB below 6) or a Dobanol ^{R} 45-7 (HLB = 11.6) and a Dobanol 23-3 (HLB = 8.1).

The preferred making of the preferred emulsions of the present invention includes: (i) premixing the hydrophobic surfactant with the aliphatic diacyl peroxide and other non-water miscible ingredients if present, like the bleach activator; (ii) premixing the hydrophilic surfactant with water and subsequently adding other water-soluble ingredients present like the second

peroxygen bleach, e.g., hydrogen peroxide; (iii) trimming the pH to preferred value; (iv) mixing the hydrophilic and the hydrophobic phase. It is important that during the mixing of the two phases, the emulsions be constantly kept under stirring under relatively low stirring energies, preferably 30 minutes at 550 rpm, most preferably 30 minutes at 450 rpm.

In the embodiment of the present invention where the compositions are formulated as emulsions said compositions are opaque. In centrifugation examination, it was observed that said emulsions herein showed no phase separation after 15 minutes at 6000 rpm. Under microscopic examination, said emulsions appeared as a dispersion of droplets in a matrix.

In the embodiment of the present invention where the compositions of the present invention are formulated as microemulsions, said bleaching microemulsions according to the present invention comprise a hydrophilic surfactant system comprising at least two different surfactants like a nonionic surfactant and an anionic surfactant.

Suitable hydrophilic surfactants to be used herein are those hydrophilic surfactants mentioned herein. A key factor in order to stably incorporate for example the bleach activator in said microemulsions is that at least one of said surfactants of the hydrophilic surfactant system must have a different HLB value to that of the bleach activator. Indeed, if all said surfactants had the same HLB value as that of the activator, a continuous single phase might be formed, thus lowering the chemical stability of the bleach/bleach activator system. Preferably, at least one of said surfactants has an HLB value which differs by at least 1.0 HLB unit, preferably 2.0 to that of said bleach activator.

Suitable anionic surfactants to be used herein include water-soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium

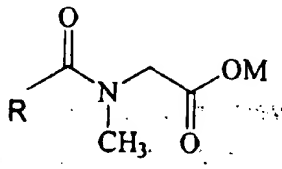
cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12-16} are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-$C_{18}E(1.0)M$, C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-$C_{18}E(2.25)M$, C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate C_{12}-$C_{18}E(3.0)$, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate C_{12}-$C_{18}E(4.0)M$, wherein M is conveniently selected from sodium and potassium.

Other anionic surfactants useful for detersive purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary or secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14-16} methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol

sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Other suitable anionic surfactants to be used herein also include acyl sarcosinate or mixtures thereof, in its acid and/or salt form, preferably long chain acyl sarcosinates having the following formula:



wherein M is hydrogen or a cationic moiety and wherein R is an alkyl group of from 11 to 15 carbon atoms, preferably of from 11 to 13 carbon atoms. Preferred M are hydrogen and alkali metal salts, especially sodium and potassium. Said acyl sarcosinate surfactants are derived from natural fatty acids and the amino-acid sarcosine (N-methyl glycine). They are suitable to be used as aqueous solution of their salt or in their acidic form as powder. Being derivatives of natural fatty acids, said acyl sarcosinates are rapidly and completely biodegradable and have good skin compatibility.

Accordingly, particularly preferred long chain acyl sarcosinates to be used herein include C_{12} acyl sarcosinate (i.e. an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 11 carbon atoms) and C_{14} acyl sarcosinate (i.e. an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 13 carbon atoms). C_{12} acyl sarcosinate is commercially available, for example, as Hamposyl L-30® supplied by Hampshire. C_{14} acyl sarcosinate is commercially available, for example, as Hamposyl M-30® supplied by Hampshire.

Suitable other hydrophilic nonionic surfactants for use in the microemulsions herein include the hydrophilic nonionic surfactants as defined hereinbefore for the emulsions.

The preferred making of the microemulsions of the present invention includes premixing the surfactants with water and subsequently adding the other ingredients including the aliphatic diacyl peroxide, the second peroxygen bleach, e.g., hydrogen peroxide, and other ingredients like a bleach activator if present. Irrespective of this preferred order of addition, it is important that during the mixing of the ingredients, the microemulsions be constantly kept under stirring under relatively high stirring energies, preferably 30 minutes at 750 rpm, most preferably 30 minutes at 1000 rpm.

In the embodiment of the present invention where the compositions are formulated as microemulsions said compositions are macroscopically transparent in the absence of opacifiers and dyes. In centrifugation examination, it was observed that said microemulsions herein showed no phase separation after 15 minutes at 6000 rpm. Under microscopic examination, said microemulsions appeared as a dispersion of droplets in a matrix. We have observed that the particles had a size which is typically around or below 3 micron diameter.

The bleaching compositions of the present invention, especially those formulated in the form of emulsions or microemulsions are chemically stable. By "chemically stable" it is meant herein that said composition of

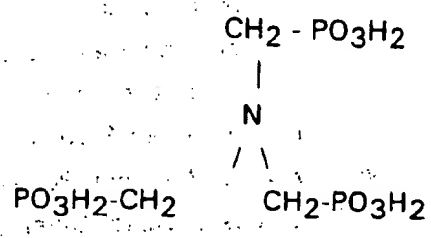
the present invention comprising said aliphatic diacyl peroxide and said second peroxygen bleach does not undergo more than 10% available oxygen loss at 50°C in 2 weeks. The concentration of available oxygen can be measured by chemical titration methods known in the art, such as the iodimetric method, the permanganometric method and the cerimetric method. Said methods and the criteria for the choice of the appropriate method are described for example in "Hydrogen Peroxide", W. C. Schumb, C. N. Satterfield and R. L. Wentworth, Reinhold Publishing Corporation, New York, 1955 and "Organic Peroxides", Daniel Swern, Editor Wiley Int. Science, 1970. Alternatively, the stability of said compositions may also be evaluated by a bulging test method.

Accordingly, said bleaching compositions of the present invention may be packaged in a given deformable container/bottle without compromising the stability of said container/bottle comprising it upon standing, for long periods of time.

Suitable chelating agents to be used herein include chelating agents selected from the group of phosphonate chelating agents, amino carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, and further chelating agents like glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid, or mixtures thereof. Chelating agents when used, are typically present herein in amounts ranging from 0.001% to 5% by weight of the total composition and preferably from 0.05% to 2% by weight.

Suitable phosphonate chelating agents to be used herein may include ethydronic acid as well as amino phosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates. Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

The most preferred phosphonate chelating agent to be used herein is aminotri(methylene phosphonic acid), herein referred to as ATMP. Indeed, it has been found that the addition of ATMP, i.e. the compound of formula :



in a liquid composition of the present invention considerably reduces the damage otherwise associated with the pretreatment of fabrics with peroxygen bleach-containing compositions, especially those fabrics which contain metal ions, such as copper, iron, chromium, and manganese.

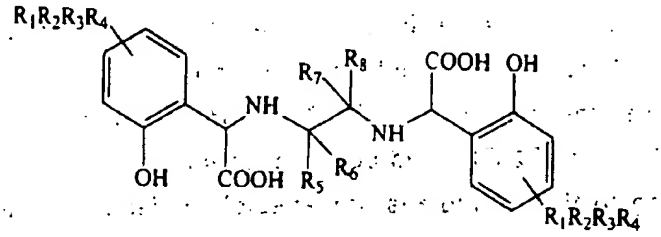
Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'- disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'- disuccinic acids is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine di-acetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance,

commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

Another preferred chelating agent for use herein is of the formula:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of -H, alkyl, alkoxy, aryl, aryloxy, -Cl, -Br, $-NO_2$, -C(O)R', and $-SO_2R''$; wherein R' is selected from the group consisting of -H, -OH, alkyl, alkoxy, aryl, and aryloxy; R'' is selected from the group consisting of alkyl, alkoxy, aryl, and aryloxy; and R_5, R_6, R_7, and R_8 are independently selected from the group consisting of -H and alkyl.

Particularly preferred chelating agents to be used herein are ATMP, diethylene triamine methylene phosphonate, ethylene N,N'-disuccinic acid, diethylene triamine pantaacetate, glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid or mixtures thereof and highly preferred is ATMP.

Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anysole, benzoic acid, toluic acid, catechol, t-butyl catechol; benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, n-propyl-gallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Radical scavengers when used, are typically present herein in amounts ranging from

0.001% to 2% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

The presence of chelating agents, especially ATMP, and/or radical scavengers allows to contribute to the safety profile of the compositions of the present invention suitable for pretreating a soiled colored fabric upon prolonged contact times before washing said fabric.

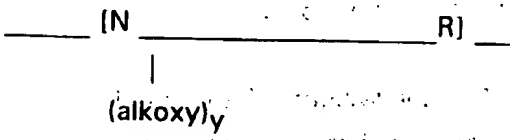
The compositions of the present invention may further comprise up to 10%, preferably from 2% to 4% by weight of the total composition of an alcohol according to the formula HO - CR'R" - OH, wherein R' and R" are independently H or a C_2-C_{10} hydrocarbon chain and/or cycle. Preferred alcohol according to that formula is propanediol. Indeed, we have observed that these alcohols in general and propanediol in particular also improve the chemical stability of the compositions, i.e. lower the decomposition of the bleaches and the bleach activator if present. In addition, said alcohols lower the surface tension of the product, thus preventing superficial film or gel formation. Thus, said alcohols improve the aesthetics of the compositions herein. It is believed that the chemical stabilising effect of said alcohols is twofold. Firstly, they may work as radical scavengers and secondly, they may interact with the bleaches, e.g., hydrogen peroxide, preventing or limiting hydrolysis, therefore reducing the rate of peroxide decomposition. It is believed that this improvement in chemical stability obtained by said alcohols is matrix independent.

Other stabilizers like inorganic stabilizers may be used herein. Examples of inorganic stabilizers include sodium stannate and various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate.

The compositions according to the present invention may further comprise a foam suppressor such as 2-alkyl alkanol, or mixtures thereof, as an optional ingredient. Particularly suitable to be used in the present invention are the 2-alkyl alkanols having an alkyl chain comprising from 6 to 16 carbon atoms, preferably from 8 to 12 and a terminal hydroxy group, said alkyl chain being substituted in the α position by an alkyl chain comprising from 1 to 10 carbon atoms, preferably from 2 to 8 and more preferably 3 to 6. Such suitable compounds are commercially available, for instance, in the

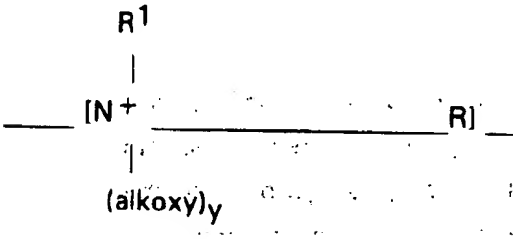
Isofol® series such as Isofol® 12 (2-butyl octanol) or Isofol® 16 (2-hexyl decanol). Typically, the compositions of the present invention comprise up to 2 % by weight of the total composition of a 2-alkyl alkanol, or mixtures thereof, preferably from 0.05 % to 1.5 % and more preferably from 0.1 % to 0.8 %.

The compositions according to the present invention may further comprise a soil suspending polyamine polymer or mixtures thereof, as optional ingredient. Any soil suspending polyamine polymer known to those skilled in the art may also be used herein. Particularly suitable polyamine polymers for use herein are polyalkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units :



Amine form

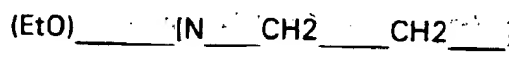
and



Quaternized form

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R^1 may be a C_1-C_{20} hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably from 10-20; n is an integer of at least 2, preferably from 2-20, most preferably 3-5; and X^- is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula :



(EtO)y (EtO)y

when y = 2-30. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular ethoxylated tetraethylenepentamine, and quaternized ethoxylated hexamethylene diamine.

It has surprisingly been found that said soil suspending polyamine polymers contribute to the benefits of the present invention, i.e., that when added on top of said aliphatic diacyl peroxide, they further improve the stain removal performance of a composition comprising them, especially under laundry pretreatment conditions, as described herein. Indeed, they allow to improve the stain removal performance on a variety of stains including greasy stains, enzymatic stains, clay/mud stains as well as on bleachable stains.

Typically, the compositions comprise up to 10% by weight of the total composition of such a soil suspending polyamine polymer or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.3% to 2%.

The compositions herein may also comprise other polymeric soil release agents known to those skilled in the art. Such polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibres, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibres and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is

bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C_4-C_6 alkylene or oxy C_4-C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1-C_4 alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 1 to about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C_4-C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2CH_2O$-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, co-polymeric blocks of ethylene terephthalate or propylene terephthalate with

polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C_1-C_4 alkyl and C_4 hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft co-polymers of poly(vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a co-polymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units which contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are fully described in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents

include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof. See U.S. Pat. No. 5,415,807, issued May 16, 1995, to Gosselink et al.

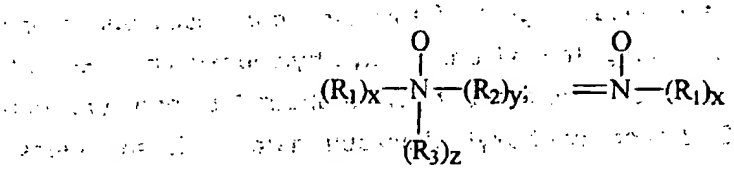
If utilised, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one dyed surface to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, co-polymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight

of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R\text{-}A_x\text{-}P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1, R_2, R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block co-polymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups

present in the polyamine oxide polymer can be varied by appropriate co-polymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polym rization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO". The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Co-polymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI co-polymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These co-polymers can be either linear or branched.

The present invention compositions may also employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

If high sudsing is desired, suds boosters such as C_{10}-C_{16} alkanolamid s can be incorporated into the compositions, typically at 1%-10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as $MgCl_2$, $MgSO_4$, and the like, can be added at levels of, for example, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Any optical brighteners, fluorescent whitening agents or other brightening or whitening agents known in the art can be incorporated in the instant compositions when they are designed for fabric treatment or laundering, at levels typically from about 0.05% to about 1.2%, by weight, of the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acids, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocyclic brighteners, this list being illustrative and non-limiting. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stil- benes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-napth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See

also U.S. Patent 3,646,015, issued February 29, 1972, to Hamilton. Anionic brighteners are typically preferred herein.

If desired, compositions herein may additionally incorporate a catalyst or accelerator to further improve bleaching or soil removal. Any suitable bleach catalyst can be used. For detergent compositions used at a total level of from about 1,000 to about 5,000 ppm in water, the composition will typically deliver a concentration of from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 50 ppm, or less, of the catalyst species in the wash liquor.

Bleach catalysts may also be used herein. Typical bleach catalysts comprise a transition-metal complex, for example one wherein the metal co-ordinating ligands are quite resistant to labilization and which does not deposit metal oxides or hydroxides to any appreciable extent under the typically alkaline conditions of washing. Such catalysts include manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; preferred examples of these catalysts include $Mn^{IV}_2(\mu\text{-}O)_3(TACN)_2\text{-}(PF_6)_2$, $Mn^{III}_2(\mu\text{-}O)_1(\mu\text{-}OAc)_2(TACN)_2(ClO_4)_2$, $Mn^{IV}_4(\mu\text{-}O)_6(TACN)_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4\text{-}(\mu\text{-}O)_1(\mu\text{-}OAc)_2\text{-}(TACN)_2\text{-}(ClO_4)_3$, $Mn^{IV}\text{-}(TACN)\text{-}(OCH_3)_3(PF_6)$, and mixtures thereof wherein TACN is trimethyl-1,4,7-triazacyclononane or an equivalent macrocycle; though alternate metal-co-ordinating ligands as well as mononuclear complexes are also possible and monometallic as well as di- and polymetallic complexes and complexes of alternate metals such as iron or ruthenium are all within the present scope. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Transition metals may be precomplexed or complexed *in-situ* with suitable donor ligands selected in function of the choice of metal, its oxidation state

and the denticity of the ligands. Other complexes which may be included herein are those of U.S. Application Ser. No. 08/210,186, filed March 17, 1994.

Although the preferred application of the compositions described herein is laundry pretreatment as described hereinbefore, the compositions of the present invention may also be used as a laundry detergent or as a laundry detergent booster and as a household cleaner in the bathroom or in the kitchen.

The compositions of the present invention suitable for pretreating fabrics can be packaged in a variety of containers including conventional bottles, bottles equipped with roll-on, sponge, brusher or sprayers.

The present invention will be further illustrated by the following examples.

Examples

The following compositions were made by mixing the listed ingredients in the listed proportions (weight % unless otherwise specified).

Compositions (weight %)	I	II	III	IV	V	VI	VII	VIII
Dobanol® 45-7	6.4	6.4	6.4	-	-	6.0	1.5	3.0
Dobanol® 23-3	8.6	8.6	8.6	-	-	-	1.5	-
Dobanol® 23-6.5	-	-	-	2.0	-	6.0	-	-
C25-AE-2.5-S	-	4.0	9.0	12.0	6.0	6.0	1.5	3.0
ATC*	-	3.5	3.5	3.5	3.5	3.5	-	-
H_2O_2	4.0	4.0	4.0	6.0	6.0	6.0	7.0	7.0
Dilauroyl peroxide	0.3	0.5	1.0	0.5	0.5	1.0	0.3	0.5
Ethoxylated (15-18) tetraethylene pentaimine	-	0.5	-	-	-	-	-	-

Water and minors	----------up to 100%----------
H2SO4 up to pH 4	

Compositions (weight %)	IX	X	XI	XII	XIII	XIV	XV	XVI
Dobanol® 45-7	6.4	6.4	6.4	-	-	6.0	1.5	3.0
Dobanol® 23-3	8.6	8.6	8.6	-	-	-	1.5	-
Dobanol® 23-6.5	-	-	-	2.0	-	6.0	-	-
C25-AE-2.5-S	-	4.0	9.0	12.0	6.0	6.0	1.5	3.0
ATC*	-	3.5	3.5	3.5	3.5	3.5	-	-
H_2O_2	4.0	4.0	4.0	6.0	6.0	6.0	7.0	7.0
Didecanoyl peroxide	0.3	0.5	1.0	0.5	0.5	1.0	0.3	0.5
Water and minors	----------up to 100%----------							
H2SO4 up to pH 4								

* ATC is acetyl triethyl citrate.

Dobanol ® 23-3 is a C12-C13 nonionic ethoxylated surfactant with HLB of 8.1.

Dobanol ® 23-6.5 is a C12-C13 nonionic ethoxylated surfactant with HLB of 11.9.

Compositions I, IV,V,VI, IX,XII,XIII and XIV are microemulsions according to the present invention. Compositions II,III,X and XI are emulsions according to the present invention. Compositions VII, VIII, XV and XVI are solutions according to the present invention.

Excellent stain removal performance is obtained on a variety of stains including carotenoid-type stains like spaghetti sauce, bleachable stains like tea and enzymatic stains like grass, blood, when pretreating soiled fabrics with compositions I to XVI, as described above, e.g., when leaving said liquid compositions to act neat onto the fabrics for a contact period of about 5 minutes, before washing said fabrics, with limited color damage.

What is claimed is:

1. A process of bleaching a fabric with a liquid composition comprising an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, or mixtures thereof, said process comprising the steps of applying said composition in its neat form onto at least a portion of said fabric, before said fabric is washed.

2. A process according to claim 1 wherein said composition remains in contact with at least a portion of said fabric for a period of time of 1 minute to 1 hour, preferably 1 minute to 30 minutes, and more preferably 2 minutes to 10 minutes, before said fabric is washed.

3. A process according to any of the preceding claims wherein said composition further comprises a second peroxygen bleach or mixtures thereof.

4 A process according to any of the preceding claims wherein said composition comprises from 0.05% to 10% by weight of the total composition of said aliphatic diacyl peroxide, or mixtures thereof, and from 0.01% to 10% by weight of said second peroxygen bleach or mixtures thereof.

5. A liquid bleaching composition suitable for pretreating fabrics, having a pH of from 0 to 6 and comprising from 0.05% to 10% by weight of the total composition of an aliphatic diacyl peroxide having the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 6 to 20 carbon atoms, and from 0.01% to 10% by weight of the total composition of a second peroxygen bleach or mixtures thereof.

6. A composition according to claim 5 or process according to any of the claims 1 to 4, wherein said aliphatic diacyl peroxide has the general formula R-C(O)-O-O-(O)C-R1, wherein R and R1 can be the same or different and are linear or branched aliphatic groups having from 4 to 18 carbon atoms, preferably from 6 to 16 and more preferably 8 to 14.

7. A composition or process according to any of the preceding claims wherein said composition comprises from 0.1% to 3% by weight of the total composition of said aliphatic diacyl peroxide, or mixtures thereof, preferably from 0.3% to 2%, and more preferably from 0.5% to 1%.

8. A composition or process according to any of the preceding claims wherein said second peroxygen bleach is hydrogen peroxide or a water-soluble source thereof, or mixtures thereof.

9. A composition or process according to any of the preceding claims wherein said composition comprises from 0.5% to 8% by weight of the total composition of said second peroxygen bleach, or mixtures thereof, preferably from 2% to 8%, and more preferably from 4% to 7%.

10. A composition or process according to any of the preceding claims wherein said composition further comprises a bleach activator, preferably at al level of from 0.01% to 10% by weight of the total composition, more preferably from 0.5% to 10% and most preferably from 3% to 7%.

11. A composition or process according to claim 10 wherein said bleach activator is selected from the group consisting of acetyl triethyl citrate, tetracetyl ethylene diamine, sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid, nonylamide of peroxyadipic acid, n-nonanoyloxybenzenesulphonate, N-acyl caprolactam, substituted and unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam, pentanoyl caprolactam and mixtures thereof, and preferably is acetyl triethyl citrate.

12. A composition or process according to any of the preceding claims wherein said composition is formulated as a microemulsion or an emulsion.

13. A composition or process according to any of the preceding claims, which has a pH of from 1 to 6, preferably of from 2 to 6, and more preferably of from 3 to 5.

Interna il Application No
PCT/US 96/14758

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/39 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 08 100 196 A (KAO CORP) 16 April 1996 see claims 1,2; examples 4,6; table 1 ---	1-13
X	WO 93 07086 A (PROCTER & GAMBLE) 15 April 1993 see page 4, paragraph 2 - paragraph 3; claims; example 4 see page 42, last paragraph - page 44, paragraph 1 -----	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 February 1997	28.02.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Loiselet-Taisne, S

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INTERNATIONAL SEARCH REPORT

...formation on patent family members

Interna ...l Application No
PCT/US 96/14758

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A-8100196	16-04-96	NONE	
WO-A-9307086	15-04-93	EP-A- 0646168	05-04-95
		JP-T- 6511223	15-12-94
		PT-A- 100921	30-11-93